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AN ESTIMATE OF THE POSSIBLE CONTRIBUTION OF BIOGENIC SOURCES TO AIRBORNE HYDROCARBON CONCENTRATIONS

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The importance of plants as sources of photoreactive hydrocarbons, oxidant precursors, is widely discussed (Coffey and Westberg, 1977). The two main questions appear to be: (1) are natural hydrocarbons emissions large enough to result in significant atmospheric concentrations and (2) do naturally emitted hydrocarbons contribute significantly to ozone formation? This note addresses the first question.

Emission rates for specific hydrocarbon species and total nonmethane hydrocarbons have been measured for several vegetation types (e.g. Table 1). Also, the influence of environmental factors such as light intensity and temperature on emission rates has been studied (Kamiyama *et al.*, 1978; Tingey *et al.*, 1978a, b).

Ordinarily the movement of air in the atmosphere dilutes pollutants emitted into it to concentrations below levels considered dangerous, however let us consider those occasions when weather is dominated by a slowly moving anticyclone, when wind speeds are small and when vertical mixing is inhibited by the stability of the overlying air. Under these conditions, in order to make a rough estimate of concentrations of biogenically-produced hydrocarbons which could occur we can use a simple box model (e.g., Peterson 1978):

$$\frac{1}{x}\frac{dx}{dt} = \frac{Q}{xh} - k,$$

where

x is the spatial average concentration,
Q is the spatial average source strength,
h is the mixing height,
k is the rate constant for the transformation or decay (ozonolysis or photoxidation) of the material under consideration, and
t is time.

This model is appropriate for sources distributed over a large area or when the wind speed is small.

* On assignment from the National Oceanic and Atmospheric Administration.

Table 1. Measured hydrocarbon emission rates from various vegetation types

Vegetation type	Compounds emitted	Emission rates $\mu g\ g^{-1}$ dry wt h^{-1}	Emission rates $\mu g\ m^{-2}\ h^{-1}$	Reference
Cryptomeria	Monoterpene	3	1500*†	Kamiyama *et al.*, 1978
Pinus elliotti	Monoterpene	6.6	3300*†	Tingey *et al.*, 1978b
Pinus taeda	α-pinene		2760†	Arnts *et al.*, 1978
Quercus virginian	Isoprene	33	16500*†	Tingey *et al.*, 1978a
Citrus	Total non-methane hydrocarbons		1500	Zimmerman, 1977
Mangrove	Total non-methane hydrocarbons		275	Zimmerman, 1977
Palmetto	Total non-methane hydrocarbons		4090	Zimmerman, 1977
Unimproved pastures	Total non-methane hydrocarbons		301	Zimmerman, 1977

* Data were converted to an area base by assuming that biomass value of 500 $g\ m^{-2}$. This value is similar to that reported by Whittaker and Marks (1975).

† Emission rates were determined at 30°C.

The emission rates listed are measured emission rates, some under field and some under laboratory conditions. They may or may not be representative of typical emissions from the particular species.

Values of model variables were chosen to represent values that can occur under suitable environmental conditions. The diurnal emission rates (Fig. 1A) of monoterpenes, primarily α and β pinene, and isoprene were calculated for a typical summer day in the southeastern United States (Tingey, 1978a, b). A diurnal variation in mixing height which might occur under reasonably stagnant conditions was assumed (Fig. 1B). Grimsrud *et al.* (1975) measured the rate constants for the photoxidation and ozonolysis (ozonolysis measured at 30 nl l^{-1} ozone concentration) of several monoterpenes and isoprene in the laboratory under simulated atmospheric conditions. The half-lives (equal to 0.69/k) for first-order or pseudo-first-order reactions of α and β pinene and isoprene are approx equal and estimated at less than 1 h during the day and about 1.5 h at night. Half-lives are shorter during the day when both ozonolysis and photoxidation reactions occur. The ozonolysis and photoxidation rates are approx equal for α and β pinene and isoprene (Grimsrud *et al.*, 1975). A diurnally varying rate constant was constructed based on these data (Fig. 1C).

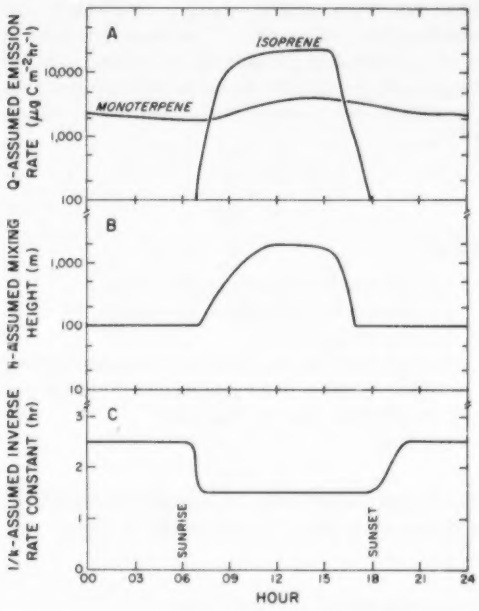

Fig. 1. Values of variables used to estimate a possible diurnal cycle of the airborne concentration of biogenically produced hydrocarbons.

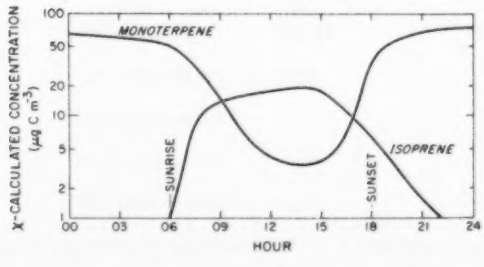

Fig. 2. Estimated diurnal cycle of the airborne concentration of monoterpene and isoprene for a simulated environment which may be typical of summertime southeastern United States.

Possible diurnal variations of concentrations of monoterpenes and isoprene (Fig. 2) were estimated using the box model given the set of conditions shown in Fig. 1. Under these conditions the model calculations indicate that the isoprene concentration should increase during daylight hours, reaching a maximum at mid-afternoon, and decrease after dark. It should approach zero during the night because there are no significant isoprene emissions then and ozonolysis reactions proceed. In contrast, the monoterpenes should have their highest concentrations during the night and lowest during the day when the rates of dilution, photoxidation and ozonolysis are the highest. Monoterpene emission rates are considerably smaller than the midday isoprene emission rate (Fig. 1A) but the concentrations of the monoterpenes during the early morning and evening hours can be larger than even the midday concentration of isoprene because monoterpenes continue to be emitted at night when atmospheric mixing is often minimal and decay reactions are slow.

The set of conditions (Fig. 1) used for making the estimates of concentrations shown in Fig. 2 are not unrealistic for those meteorological situations where the weather is dominated by a slowly moving anticyclone. It is possible for the ventilation conditions to be even more restrictive although most of the time they should be less restrictive. The results of the calculations suggest that under certain conditions of atmospheric stagnation in warm environments, such as during the summer in the southeastern United States, the biogenic emissions of hydrocarbons may contribute significantly to the total airborne hydrocarbon concentration.

The estimates presented here are based on emission rates measured under controlled conditions and on what little is known about the fate in the atmosphere of biogenically-produced hydrocarbons. Whether or not concentrations of these biogenically-produced hydrocarbons ever approach or exceed the concentrations estimated here is not known. We only point out that concentrations of the order of 10–100 $\mu g\ m^{-3}$ are not inconsistent with what is known about the emission rates and reactivity of these compounds. There is some evidence (Whitby and Coffey, 1977) that concentrations in this range do occur in the atmosphere. Even if concentrations of the magnitude we estimate do occur it does not follow that biogenic sources of hydrocarbons contribute significantly to ozone formation. Reactive hydrocarbons are a sink for ozone and only in the presence of sufficient quantities of nitrogen oxides and sunlight is ozone produced. It appears that most nitrogen oxides

are anthropogenic in origin so that even though large quantities of reactive hydrocarbons are emitted by plants, significant sources of nitrogen oxides may not be available for ozone production.

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